

U.S. NON-PROVISIONAL PATENT APPLICATION

ENTITLED:

**ALPHA OLEFIN MONOMER PARTITIONING AGENTS
FOR DRAG REDUCING AGENTS AND METHODS OF
FORMING DRAG REDUCING AGENTS USING
ALPHA OLEFIN MONOMER PARTITIONING AGENTS**

By

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RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/253,279, filed November 27, 2000.

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BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates to partitioning agents, or coating agents, for use in connection with drag reducing agents, and in particular, alpha olefin monomer partitioning agents used in methods 10 for improving flow of hydrocarbons through conduits, particularly pipelines. The invention also relates to methods for making improved drag reducing agents.

2. Description Of Related Art

Generally speaking, the flow of liquid in a conduit, such as a pipeline, results in frictional 15 energy losses. As a result of this energy loss, the pressure of the liquid in the conduit decreases along the conduit in the direction of the flow. For a conduit of fixed diameter, this pressure drop increases with increasing flow rate. When the flow in the conduit is turbulent (Reynold's number greater than about 2100), certain high molecular weight polymers can be added to the liquid flowing 20 through the conduit to reduce the frictional energy losses and alter the relationship between pressure drop and flow rate. These polymers are sometimes referred to as drag reducing agents ("DRAs"), and they interact with the turbulent flow processes and reduce frictional pressure losses such that the pressure drop for a given flow rate is less, or the flow rate for a given pressure drop is greater. Because DRAs reduce frictional energy losses, increase in the flow capability of pipelines, hoses and other conduits in which liquids flow can be achieved. DRAs can also decrease the cost of pumping 25 fluids, the cost of equipment used to pump fluids, and provide for the use of a smaller pipe diameter for a given flow capacity. Accordingly, an ongoing need exists to formulate improved drag reducing materials.

While various polymerization methods, reactants, and partitioning agents have been published in the patent literature, many of those methods utilize expensive partitioning agents that

adversely effect the hydrocarbons transported through the conduit. In many, if not all, instances, these partitioning agents remain in the hydrocarbon stream thereby fouling the hydrocarbon and decreasing the number of uses of the hydrocarbon and/or the effectiveness of the use of the hydrocarbon. In certain aspects, the present invention overcomes one or more of the above-5 mentioned shortcomings.

While various partitioning agents have been used in connection with certain drag reducing agents, the inventors are not aware of any patents or publications showing alpha olefin monomers as being used as partitioning agents in connection with drag reducing agents (DRAs). For example, U.S. Patents Nos. 4,720,397; 4,789,383; 4,826,728; 4,837,249; 5,244,937; 5,449,732; 5,504,131; 10 5,504,132; 5,539,044; and 6,172,151 disclose certain partitioning agents, but do not disclose or suggest the alpha olefin monomer partitioning agents of the present invention.

SUMMARY OF INVENTION

In accordance with the invention the foregoing advantages have been achieved through the 15 present process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent, the process comprising: contacting alpha olefin monomers with a catalyst in a reactant mixture, wherein the reactant mixture includes at least one alpha olefin monomer partitioning agent; and polymerizing the alpha olefin monomers, wherein during the polymerization, at least a portion of the alpha olefin monomer polymerize in the reactant mixture 20 to provide a polyalphaolefin.

A further feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the catalyst may be a transition metal catalyst. Another feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the transition metal catalyst may be a Ziegler-Natta catalyst. An additional feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the Ziegler-Natta catalyst may be titanium trichloride. Still another feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the reactant mixture may include at least one co-catalyst. 25

A further feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the at least one co-catalyst may be selected from the group consisting of alkylalumininoxanes, halohydrocarbons, diethylaluminum chloride, and dibutylaluminum chloride. Another feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the alpha olefin monomers may comprise homopolymers, terpolymers or copolymers. An additional feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the alpha olefin monomers may comprise co-polymers of 1-hexene and 1-dodecene alpha olefins or co-polymers of 1-octene and 1-tetradodecene alpha olefins. Still another feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the polyalphaolefin may be an ultra-high molecular weight polyalphaolefin having an inherent viscosity of at least about 10 deciliters per gram and is amorphous with substantially no crystalline particles. A further feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the at least one alpha olefin monomer partitioning agent may be selected from the group consisting of C₂₀ - C₆₀ alpha olefin monomers.

In accordance with the invention the foregoing advantages have also been achieved through the present drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent.

A further feature of the drag reducing agent is that the at least one alpha olefin monomer partitioning agent may be selected from the group consisting of C₂₀ - C₆₀ alpha olefin monomers.

In accordance with the invention the foregoing advantages have also been achieved through the present drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent formed by contacting alpha olefin monomers with a catalyst in a reactant mixture having at least one alpha olefin monomer partitioning agent; and polymerizing the alpha olefin monomers, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin.

In accordance with the invention the foregoing advantages have also been achieved through the present drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer

partitioning agent formed by contacting alpha olefin monomers with a catalyst in a reactant mixture; polymerizing the alpha olefin monomers, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin; and mixing the polyalphaolefin with at least one alpha olefin monomer partitioning agent.

5 In accordance with the invention the foregoing advantages have also been achieved through the present process for reducing drag in a conduit, comprising: forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent, wherein the drag reducing agent is formed by contacting alpha olefin monomers with a catalyst in a reactant mixture having at least one alpha olefin monomer partitioning agent; polymerizing the alpha olefin
10 monomers, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin; and introducing the drag reducing agent into the conduit.

15 In accordance with the invention the foregoing advantages have also been achieved through the present process for reducing drag in a conduit, comprising: forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent, wherein the drag reducing agent is formed by contacting alpha olefin monomers with a catalyst in a reactant mixture; polymerizing the alpha olefin monomers, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin; mixing the polyalphaolefin with at least one alpha olefin monomer partitioning
20 agent; and introducing the drag reducing agent into the conduit.

25 In accordance with the invention the foregoing advantages have also been achieved through the present process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent, the process comprising: contacting alpha olefin monomers with a catalyst in a reactant mixture; polymerizing the alpha-olefin monomers, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin; and mixing the polyalphaolefin with at least one alpha olefin partitioning agent.

A further feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the at least one alpha

olefin partitioning agent may be selected from the group consisting of C₂₀ - C₆₀ alpha olefin monomers. Another feature of the process for forming a drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent is that the process may further comprise the step of cryogrinding the polyalphaolefin and at least one alpha olefin partitioning agent.

The alpha olefin monomer partitioning agents, methods of reducing drag in a conduit, and methods of forming drag reducing agents have the advantages of: decreasing the cost of production of drag reducing agents having partitioning agents; and decreasing the instances of hydrocarbon fouling caused by partitioning agents.

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DETAILED DESCRIPTION OF THE INVENTION

The following detailed description refers to certain details and specific aspects of the invention, including specific embodiments and examples of the invention. Also, for purposes of better understanding the invention, certain terms will now be explained and defined. It is to be understood that the invention is not limited or restricted to the specific examples and embodiments described below, which are included to assist a person skilled in the art in practicing the invention. On the contrary, it is intended to cover all alternatives, modifications, and equivalents, as may be included within the spirit and scope of the invention as defined by the appended claims.

The term "drag reducing agent" (DRA) as used herein refers to a composition that includes at least the formed polyalphaolefin polymer and at least one alpha olefin monomer partitioning agent. The term "polyalphaolefin" refers to the polymer material formed by the polymerization of alpha olefin monomers, and is broadly construed to include not only the polymer in its final form, but also any intermediate polymers being formed, sometimes referred to as "oligomers." Preferably, the polyalphaolefin polymer is amorphous, i.e., the polyalphaolefin has no crystalline structures, or habits, existing in a single phase with substantially no solid particles, and has an ultra-high molecular weight and inherent viscosity of 10 dL/g or greater.

"Ultra-high molecular weight," means a molecular weight corresponding to an inherent viscosity of at least about 10 dL/g. Because of the extremely high molecular weight of the DRA polymer, it is difficult to reliably and accurately measure the actual molecular weight, but inherent

viscosity provides a useful approximation of molecular weight. "Inherent viscosity" is measured using a Cannon-Ubbelohde four bulb shear dilution viscometer (0.1 g polymer/100 ml toluene at 25°C). Inherent viscosities are calculated for each of the four bulbs. The viscosities are then plotted as a function of shear rate. The plot is then used to determine the inherent viscosity at a shear rate 5 of 300 sec-1. It is contemplated that an inherent viscosity of 10 dL/g corresponds roughly to a molecular weight of at least about 10 or 15 million. Preferably, the ultra-high molecular weight polyalphaolefins have molecular weights even higher, e.g., greater than 25 million. The polyalphaolefins formed preferably have a narrow molecular weight distribution. Because different assumptions about the properties of the polyalphaolefin can yield different estimates of molecular 10 weights, the inventors prefer using inherent viscosity to characterize the molecular weights of their drag reducing agents.

While the polyalphaolefin polymer may be formed using any method known to persons skilled in the art (e.g., using the methods disclosed in U.S. Patents Nos. 3,692,676; 4,289,679; 15 4,358,572; 4,433,123; 4,493,903; 4,493,904; 5,244,937; 5,449,732; 5,504,131; 5,504,132; and 5,539,044, all of which are hereby incorporated by reference), the polyalphaolefin polymer is preferably made in accordance with the methods described in U.S. Patent Nos. 5,869,570 and 6,015,779, both of which are hereby incorporated by reference. Generally, the polyalphaolefin polymer is formed by contacting alpha olefin monomers, e.g., alpha olefins monomers having 2 to 20 carbon atoms, with a catalyst in a reactant mixture. Homopolymers, copolymers and terpolymers 20 may be used. Preferred alpha olefins include ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene; conjugated or unconjugated dienes such as butadiene and 1, 4-hexadiene; aromatic vinyls such as styrene; and cyclic olefins such as cyclobutene. Most preferably, the alpha olefin monomers are co-polymers of 1-hexene and 1-dodecene present in a 1:1 mole ratio; or co-polymers of 1-octene and 1-tetradecene present in a 1:1 25 mole ratio.

In one preferred embodiment, disclosed in U.S. Patent No. 6,015,779, alpha olefin monomers are contacted with a catalyst and a co-catalyst system having at least one co-catalyst. While it is contemplated that any catalyst known to persons skilled in the art may be utilized, e.g., metallocene or Ziegler-Natta catalysts, preferred catalysts include transition metal catalysts such as those catalysts

containing titanium trichloride, titanium tetrachloride or metallocene or combinations thereof. Preferably, the transition metal catalysts are non-metallocene. Titanium trichloride, which is most preferred, has been used for years in making drag reducing agents, and is preferably used in an amount ranging from at least about 100 to 1500 parts per million (ppm) based on the weight of all 5 the components, i.e., the alpha olefins, co-catalysts, and catalysts supplied to the reactor.

Co-catalysts have also been used for years to form drag reducing agents. It is contemplated that any co-catalyst known to persons skilled in the art may be included with the catalyst; however, preferred co-catalysts includes one or more co-catalyst selected from the group consisting of alkylaluminoxanes, halohydrocarbons, diethylaluminum chloride ("DEAC") and dibutylaluminum 10 chloride ("DIBAC"). As mentioned above, the process of forming the drag reducing agent may include no co-catalyst, one co-catalyst, or a plurality of co-catalysts.

The alpha olefin monomers may be polymerized at a temperature at about or less than 25°C, and preferably, at about or less than 10°C, wherein during the polymerization, at least a portion of the alpha olefin monomers polymerize in the reactant mixture to provide a polyalphaolefin. 15 Preferably, the alpha olefin monomers are polymerized at a temperature of about -5°C.

Partitioning agents, also known as coating agents, are compositions that help prohibit polyalphaolefin polymer particles from sticking together in large clumps, thereby facilitating the dispersion of the polyalphaolefin in the hydrocarbon in the conduit. The partitioning agents may be added to the reactant mixture, i.e., during polymerization, after polymerization, and/or during 20 grinding of the polyalphaolefin into fine polymer particles.

The alpha olefin monomer partitioning agents of the present invention are solid at ambient temperatures, i.e., at temperature at which polymerization occurs. In other words, the alpha olefin monomer partitioning agents have a melting point that is higher than the alpha olefin monomers that undergo polymerization. Therefore, in one specific embodiment in which the alpha olefin monomer 25 partitioning agents are included in the reactant mixture, the alpha olefin monomer partitioning agents do not undergo polymerization.

Generally, alpha olefin monomer partitioning agents that are solid at ambient temperature are C₂₀ to C₆₅ alpha olefin monomers. However, it is contemplated that solid C₁ through C₁₉ alpha olefin monomers, as well as solid C₆₆ and greater alpha olefin monomers, may also be designed to

be suitable partitioning agents of the present invention provided these alpha olefin monomers have a melting point that is higher than the temperature at which the polymerization of the alpha olefin monomers occurs.

5 In one embodiment, the alpha olefin monomer partitioning agents of the present invention are included in the reactant mixture. Because the alpha olefin monomer partitioning agents do not polymerize, they remain functional, i.e., prohibit polyalphaolefin polymer from sticking together. In this embodiment, the alpha olefin monomer partitioning agent is present in the reactant mixture in an amount ranging from at least about 10 to about 50 weight percent based upon the weight of all of the components, e.g., alpha olefin monomers, catalyst, co-catalyst(s), etc., of the reactant mixture.
10 Preferably, the alpha olefin monomer partitioning agent is present in the reactant mixture at a concentration of at least about 25 weight percent.

15 Alternatively, the alpha olefin monomer partitioning agents of the present invention may be mixed with the polyalphaolefin prior to, or during, cryogrinding as disclosed in U.S. Patents Nos. 5,244,937; 5,449,732; 5,504,131; 5,504,132; and 5,539,044. In these embodiments, the alpha olefin monomer partitioning agent is combined with the polyalphaolefin in an amount ranging from at least about 10 to about 50 weight percent based upon the weight of all of the components, e.g., polyalphaolefin, unpolymerized alpha olefin monomers, unused catalyst, unused co-catalyst(s), etc., undergoing cryogrinding. Preferably, the alpha olefin monomer partitioning agent is present at a concentration of at least about 25 weight percent.

20 Drag reducing agent slurries may be formed by mixing the drag reducing agent with at least one slurry component. Numerous slurry components are known to persons skilled in the art. Examples of suitable slurry components are disclosed in U.S. Patent Nos. 5,244,937; 5,449,732; 5,504,131; 5,504,132; and 5,539,044.

25 Additionally, dispersing agents may be included in the reactant mixture. Preferably, the dispersants of this invention do not substantially impair the polymerization process. While any dispersant known to persons skilled in the art may be utilized, examples of suitable dispersants include, alone or in combination, copolymers of polyacrylic acid; polymethacrylic acid; copolymers of polymethacrylic acid; polyethylene; copolymers of polyethylene; polynonylphenol and/or polybutylphenol, including copolymers of polynonylphenol and polybutylphenol, in combination

with ethylene oxide and/or propylene oxide; polymers and copolymers of petroleum sulfonates; and compounds containing ethylene glycol monobutyl ether. Preferred dispersants are polymers and copolymers of acrylates and methacrylates; polymers and copolymers of ethylene; polymers and copolymers produced from the polymerization of nonylphenol and butylphenol in combination with 5 ethylene oxide and/or propylene oxide; compounds or blends of compounds containing petroleum sulfonates; compounds containing ethylene glycol monobutyl ether (butyl "Cellosolve"); and CARBOPOL®, sold by B. F. Goodrich Company.

The dispersant, which may be added prior to, or during, polymerization, modifies the viscosity of the reaction mixture and disperses the partitioning agent and polymer fines, i.e., finely 10 ground polyalphaolefin particles, through out the reactant mixture. The concentration of the dispersant in the reactant mixture is preferably from about 0.5 ppm to about 50,000 ppm of the reactant mixture. Alternatively, the dispersant may be added after polymerization, before, after, or at the same time the slurry component is mixed with the drag reducing agent or polyalphaolefin to 15 form the drag reducing agent slurry. In this embodiment, the concentration of the dispersant is preferably from about 0.5 ppm to about 50,000 ppm.

Drag reducing agents comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent may be used to reduce drag in a conduit by adding the drag reducing agent to a conduit containing a hydrocarbon. Additionally, the drag reducing agent comprising a polyalphaolefin and at least one alpha olefin monomer partitioning agent may also be further 20 processed by any method known to those skilled in the art to be utilized to reduce drag in a conduit.

It is to be understood that the invention is not limited to the exact details of construction, operation, exact materials, or embodiments shown and described, as obvious modifications and equivalents will be apparent to one skilled in the art. Accordingly, the invention is therefore to be limited only by the scope of the appended claims.